Discriminating Seebeck Sensing of Molecules
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Fig. S1 | Seebeck coefficient measurements of different molecules. The peak value Seebeck coefficient and its distribution have the same sign in most molecules. This means that the Seebeck coefficient is robust against changes due to environment such as binding configuration or confirmations. Seebeck coefficient of a, benzenedithiol (BDT), dibenzenedithiol (DBDT), tribenzenedithiol (TBDT) between gold electrodes, b, 4,4'-diaminostilbene (1), bis-(4-aminophenyl)acetylene (2), 1,5- bis-(diphenylphosphino)pentane (3), 4,4'-bipyridine (4), and 1,2- di(4-pyridyl)ethylene (5), c, thiophene-1,1-dioxide with different length, d, C60, e, endohedral metallofullerenes C82 (a), Gd@C82 (b) and Ce@C82 (c), f, bipyridine and C60 versus gate voltage, and g, trimethylstannymethyl-terminated oligophenyl with different lengths.
Fig. S2 | Mn-Porphyrin molecular junction. a, Transmission coefficient of graphene/Mn-Porphyrin/graphene junctions in the absence and presence of Chlorine for a, majority (↑), b, minority (↓) spins. c, Total transmission coefficient $T = (T^\uparrow + T^\downarrow)/2$.

Fig. S3 | Mn-Porphyrin molecular junction. a, Transmission coefficient and b, the Seebeck coefficient in the absence (blue curve) and presence (yellow curve) of nitrogen gas. Although the transmission changes in the presence of $N_2$ molecule, the transport remains LUMO dominated and therefore the sign of Seebeck coefficient does not change. However, the amplitude of both Seebeck and transmission coefficients change.

The transmission coefficient of a one level system (fig. S4a) is obtained from the Breit–Wigner formula:

$$T(E) = \frac{4\Gamma_L\Gamma_R}{(E - \varepsilon_n)^2 + (\Gamma_L + \Gamma_R)^2}$$  \hspace{1cm} \text{(S1)}

where $\varepsilon_n = \lambda - \sigma_L - \sigma_R$ and $\sigma_L, \sigma_R$ and $\Gamma_L, \Gamma_R$ are real and imaginary part of self-energies, respectively. $\lambda$ is the eigenenergy of the molecular orbital shifted slightly by an amount $(\sigma_L + \sigma_R)$ due to the coupling of the orbital to the electrodes. This formula shows that when the electron resonates with the molecular orbital e.g. when $E = \varepsilon_n$, electron transmission is a maximum (blue curve in fig. S4). If a bound state (e.g. a pendant group $\varepsilon_p$) is coupled (by coupling integral $\alpha$) to a continuum of states, Fano resonances could occur. Fano resonance contains an anti-resonance followed by a resonance with an asymmetric line profile in between. Fano resonance originates from a close coexistence of resonant transmission and resonant reflection. In this case, $\varepsilon_n = \lambda - \sigma_L - \sigma_R + \frac{\alpha^2}{E - \varepsilon_p}$ in the Breit–Wigner formula (equation S1). At $E = \varepsilon_p$, electron transmission is destroyed (the electron anti-resonates with the pendant orbital) and at $E = \varepsilon_n$, the electron transmission is resonated by $\varepsilon_n$ (red curve in fig. S4).

Using the Mott formula,

$$S = -\frac{k_B^2\pi^2\tau}{3e} \times \left(\frac{dT(E)/dE}{T(E)}\right)_{E=E_F}$$  \hspace{1cm} \text{(S2)}

and the transmission coefficient of a one level system (equation S1), the Seebeck coefficient is obtained.

$$S = \frac{k_B^2\pi^2\tau}{3e} \times \frac{2(E_F - \varepsilon_n)}{(E_F - \varepsilon_n)^2 + (\Gamma_L + \Gamma_R)^2}$$  \hspace{1cm} \text{(S3)}

where $k_B$ and $T$ are Boltzmann constant and temperature, respectively. As shown in figure S4b, although the amplitude of transmission coefficients in the absence and presence of analyte are equal at electrodes Fermi energy ($E_F=0eV$), the slope of transmissions are different. Therefore, the sign of Seebeck coefficient obtained from equation S3 at room temperature changes (fig. S4c) in the presence of pendant group (analyte).
**Fig. S4 | Simplest model calculation.** a, Scattering region consist of a bound state (analyte) connected to a one level backbone is weakly coupled to the one dimensional electrodes. b, A Lorentzian like transmission coefficient is formed in the absence of analyte (blue curve). In the presence of analyte, a Fano resonance formed. Although the amplitude of transmission coefficients in the absence and presence of analyte are equal at the electrodes Fermi energy ($E=0\text{eV}$), the slope of transmissions are different. c, The Seebeck coefficient changes sign in the presence of analyte.

**Fig. S5 | Zn-Porphyrin molecular junction.** a, Transmission coefficient and b, the Seebeck coefficient in the absence (purple curve) and presence (green curve) of Cl$_2$ molecule. Due to electrostatic effect of Chlorine molecule, the transmission has slightly shifted leading to a small increase of $S$. However, the sign of $S$ is not affected.

**Supporting references**